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In re Application of:

Sato

Serial Number: 09/807,214

Group Art Unit: 1745

Filed: June 1, 2001

Examiner: Julian A. Mercado

Title: ELECTRODE STRUCTURE, ELECTRIC COMPONENTS AND  
MANUFACTURING METHOD

OFFICIAL

\*\*\*\*\*

DECLARATION BY APPLICANT REGARDING  
OVERLY BROAD RANGE AND  
UNEXPECTED RESULTS

Commissioner for Patents  
P.O. Box 1450  
Alexandria, VA 22313-1453

August 2, 2004

Commissioner:

I, Takaya Sato, being first duly sworn, on oath makes the following statement  
and declaration of facts:

I am a joint inventor of the above-identified patent application (the "subject  
application").

I am employed as chief scientist at Nissinbo Industries Inc. of Tokyo, Japan  
("Nissinbo"). I attended Shinshuu University, where I obtained a Masters

degree in Chemistry, and then I obtained my PhD from Kyoto University in 1992. I have been employed with Nisshinbo for the past nineteen years and during my time there I have been involved in significant research, development and testing in the electrochemistry and polymer fields. I have also been involved in the creation and invention of several kinds of products in the polymer and electromechanical device fields, thereby utilizing my technical experience and background. Through my experience I have become well aware of the standards and terminology used in the battery and capacitor industry and have filed patent applications in the polymer science field. Throughout my nineteen years with Nisshinbo I have filed numerous domestic, Japanese patent applications in the same field of art and have had about thirty patents issued in Japan in the same field of art. I have also filed and have had issued ten United States patent applications in the same field of art since the year.

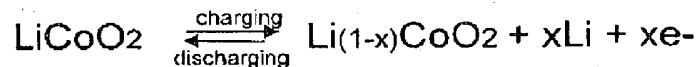
I read the office action issued on serial number 09/807,214 mailed on May 13, 2004 and conducted the experiment of using the ion-conducting polymer which is able to dissolve at least the lithium salts at a concentration of at least 0.1M (mol/l) which shows an electrical conductivity of  $10^{-8}$  S (siemens)/cm at room temperature when dissolved with the lithium salts at a concentration of at least 0.1M.

The advantages of employing this type of polymer coated on the surface of the powdered electrode active material is to shift the critical point at which thermal runaway occurs to a high temperature side. No conventional art, including Hayashi et al., teaches or suggests these limitations. In order to prove the advantages, I provide a declared experiment herewith.

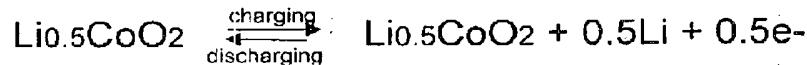
### ***Definition of Overcharging***

Although LiCoO<sub>2</sub> itself is a stable material, it becomes unstable when number of Li atoms in the molecular formula is equal to or less than 0.5, thereby categorized as being in an overcharging state, which is known to explodingly generate heat or burn when exposed to a high temperature atmosphere.

(1) A general equation expressing the reaction on a positive electrode of the lithium ion battery is:



(2) A following equation expresses the reaction of a fully charged lithium ion battery sold in a today's market:



### ***Experiment A (ion-conducting polymer coating)***

The electrode was prepared according to Example 4 (positive electrode) and Example 6 (negative electrode), and the sample battery was made according to (j) Charging/discharging tests on page 29 of the specification. As the supporting electrolyte salt 1M LiBF<sub>4</sub> in a 1:1 volumetric mixture of ethylenecarbonate and diethylenecarbonate as the nonaqueous solvent was used. The sample battery was fully charged where the active material in the positive electrode was Li<sub>0.5</sub>CoO<sub>2</sub>.

### ***Comparative Example B (polyvinylidene fluoride)***

The electrode was prepared according to Comparative Example 1

(positive electrode) and Comparative Example 2 (negative electrode), and the sample battery was made according to (j) Charging/discharging tests on page 29. As the supporting electrolyte salt 1M LiBF<sub>4</sub> in a 1:1 volumetric mixture of ethylenecarbonate and diethylenecarbonate as the nonaqueous solvent was used. The sample battery was fully charged where the active material in the positive electrode was Li<sub>0.5</sub>CoO<sub>2</sub>.

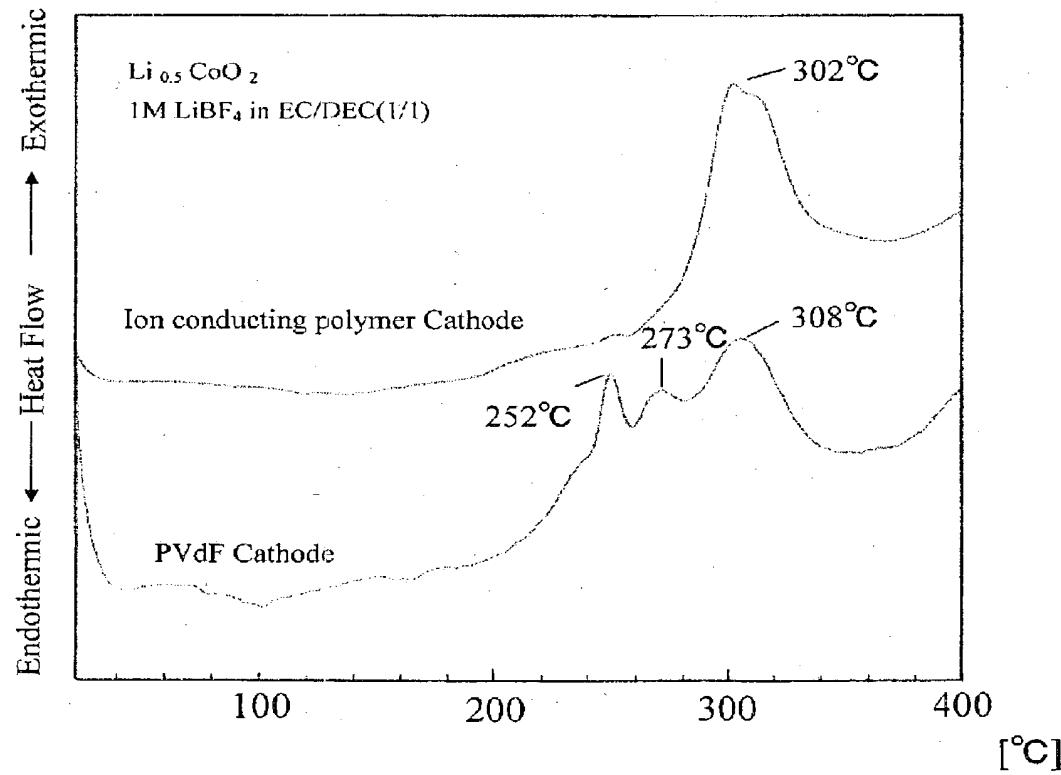
#### ***Measuring Method***

The fully charged battery was decomposed under argon atmosphere to extract the positive electrode active material (Li<sub>0.5</sub>CoO<sub>2</sub>). The extracted positive electrode active material was filled in a sealable aluminum test container to perform differential scanning calorimetry (DSC). Temperature was increased at 10°C/min to 400°C. The following graph shows the heat flow measurement which shows some heat peaks after 250°C. These are points at which thermal runaway occurs. This measurement was performed using a differential scanning calorimetry (Seiko Instruments Company Limited).

#### ***Results***

The following graph shows the thermal runaway reaction of Comparative Example B using polyvinylidene fluoride (PVdF) at 252°C while the thermal runaway reaction of Experiment A using the ion-conducting polymer coating went up to 302°C. Z. Zhang et al. explains about the experiment of measuring the thermal runaway point with respect to LiCoO<sub>2</sub> (normal state) and Li<sub>0.0</sub>14CoO<sub>2</sub> (thermal runaway point). Z. Zhang et al. J. Power Source, 70, 16(1998) which is attached hereto. Z. Zhang et al. using PVdF shows the thermal runaway point approximately equal to Comparative Example B of this

experiment. Accordingly, using the polymer type in the present invention gives significant advantages over conventional arts by offering stability and safety.



I hereby declare that all statements made herein are of my own knowledge are true and that all statements made on information and belief are believed to be true and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Takuya Sato  
Takuya Sato

August 2, 2004

Chiba, Japan



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**POWER  
SOURCES**

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## Differential scanning calorimetry material studies: implications for the safety of lithium-ion cells

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### Abstract

Differential scanning calorimetry (DSC) has been demonstrated to be a useful means of studying the reactivity of materials used in lithium-ion cells. In the present study, the reactivity of three most commonly used transition metal oxides, i.e.  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x\text{Mn}_2\text{O}_4$ , in the presence of electrolyte were investigated by DSC. The most commonly used negative electrode material, carbon ( $\text{Li}_x\text{C}_6$ ) was also studied. In the paper, relative levels of reactivity of the materials as a function of stoichiometry are reported. The implications of the results on the safety of lithium-ion cells are discussed. © 1998 Elsevier Science S.A.

**Keywords:** Lithium-ion batteries; Safety; Differential scanning calorimetry; Reactivity

### 1. Introduction

Lithium-ion technology using lithium transition metal oxide positives and carbon negatives is rapidly becoming the state-of-the-art rechargeable battery technology. A unique combination of high voltage, high energy density, excellent cycle life and moderate rate capability has made the Li-ion cell one of the leading power sources for a wide range of portable electronics applications [1]. The technology also shows promise for eventual electric-vehicle applications.

Although the replacement of metallic Li with carbon intercalation negatives significantly improved the safety of secondary Li cells, some concerns remain, particularly in view of recent problems in the field [2]. Li-ion cells are not immune to safety incidents since their thermal stability limits are finite. We have found that cells deliberately heated to high temperatures eventually undergo a thermal runaway reaction, producing very high cell temperatures, smoke and even fire [3]. This implies that under abusive conditions, the potential exists to heat a cell beyond its thermal stability limit, initiating the runaway reaction and producing a safety incident. To date, safety engineering has played a key role in mitigating potential safety prob-

lems. Techniques such as precise charge control, internal fusing and over-pressure disconnect devices have been quite successful in achieving battery safety.

From a materials point of view, the safety characteristics intrinsically depend on the stoichiometry of the metal oxide electrodes and carbon electrodes ( $x$  in  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{C}_6$  for example). The  $x$  values in the three most commonly used metal oxide materials, i.e.  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{CoO}_2$  and  $\text{Li}_x\text{Mn}_2\text{O}_4$ , have been found to have significant impact on their thermal stability at high temperatures. Thermal gravity analysis (TGA) studies of electrolyte-free  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{CoO}_2$  and  $\lambda\text{-MnO}_2$  samples have been reported [4], where small  $x$  values encouraged the decomposition of the active materials with the liberation of  $\text{O}_2$ . Even though the carbon intercalation electrode is much safer than Li metal [5], it still can react with the electrolyte and generate heat under abusive conditions, especially for large  $x$  values in  $\text{Li}_x\text{C}_6$ .

In practical cell operation, both the positive and negative electrode will undergo reactions with the electrolyte if the cell is abused. Although many companies have reported results of cell safety evaluations, data on the anode and cathode intrinsic safety properties, and their reaction mechanisms with the electrolyte have been sparse. Because of the exothermic nature of the reactions, differential scanning calorimetry (DSC) offers a convenient means of studying the reaction rates and mechanisms under controlled conditions. With this technique, samples are heated

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at a controlled rate, and the heat flow to or from the sample is measured. By comparing heat flow rates, onset temperatures and total heat generation, the effects of variables such as electrode materials, stoichiometry and electrolyte compositions on cell safety can be readily studied.

The present DSC investigation deals with the intrinsic reactivity of  $\text{Li}_x\text{NiO}_2$ ,  $\text{Li}_x\text{CoO}_2$ ,  $\text{Li}_x\text{Mn}_2\text{O}_4$ , and  $\text{Li}_x\text{C}_6$  at different  $x$  values in the presence of the electrolyte. The understanding of such reactions is essential in the design of safe, high performance Li-ion cells.

## 2. Experimental

$\text{LiNiO}_2$  was obtained from FMC,  $\text{LiCoO}_2$  from Fuji and  $\text{LiMn}_2\text{O}_4$  from Chemetals. The MCMB25-28 (meso-carbon microbeads, average particle size of 25  $\mu\text{m}$ , graphitized at 2800 °C) carbon material was purchased from Osaka Gas. Electrodes were made by slurry-coating on aluminum or copper substrates. All electrodes used polyvinylidene fluoride (PVDF) binder (Elf Atochem). Unless noted otherwise, the electrolyte used in the study was 1.0 M  $\text{LiPF}_6$  (Hashimoto) in ethylene carbonate/dimethyl carbonate (EC/DMC) (1:1 by volume). Both EC and DMC were obtained from Grant Chemical.

Sample preparation initially consisted of de-intercalation of  $\text{LiNiO}_2$ ,  $\text{LiCoO}_2$ , or  $\text{LiMn}_2\text{O}_4$  electrodes, or intercalation of carbon electrodes. This was carried out in 2325 coin cell hardware using an Li metal foil as the counter electrode at a current density of 0.1 mA/cm<sup>2</sup>. The cells were either charged (metal oxide samples) or discharged (carbon samples) to a predetermined capacity to achieve the desired stoichiometry for the materials under study. Voltage cutoffs were also used (5.0 V for cathode materials, 0.01 V for anode materials) to ensure that only intercalation reactions occurred during the sample preparation.

The coin cells were then transferred to a glove box containing an argon atmosphere, and opened. About 0.5–1.5 mg of the active materials of interest was taken, placed in aluminum DSC cells and hermetically sealed by crimping. The Li metal and separator were discarded. Unless otherwise noted, all the lithiated oxide samples had 16–26 wt.% electrolyte and the carbon samples had ~30 wt.% electrolyte. All DSC calculations were based on the overall weight of the sample. The DSC experiments were carried out on a Model DSC10 differential scanning calorimeter (TA Instruments) at a ramp rate of 10 °C/min. The temperature range utilized was from room temperature to 400 °C. Exothermic and endothermic reactions as a function of the temperature were plotted as positive and negative heat flow, respectively.

## 3. Results and discussion

The stoichiometric values of lithium nickelate, cobaltate, manganate and MCMB25-28 carbon covered in the

Table 1  
Summary of material stoichiometry values for DSC tests,  $x$  values in the indicated compounds

Material	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6
$\text{Li}_x\text{NiO}_2$	1.0	0.75	0.45	0.35	0.25	0.05
$\text{Li}_x\text{CoO}_2$	1.0	0.75	0.45	0.35	0.25	0.014
$\text{Li}_x\text{Mn}_2\text{O}_4$	1.0	0.46	0.20	0.11		
$\text{Li}_x\text{C}_6$	0	0.23	0.46	0.91		

present studies are summarized in Table 1. Fig. 1 shows the DSC curves of  $\text{Li}_x\text{NiO}_2$  plus the electrolyte for  $x$  values of 1.0 to 0.05. The  $\text{LiNiO}_2$  was quite stable over the entire temperature range, and only a small endothermic peak from 250 to 280 °C was observed. This appeared to be due to electrolyte endothermic reactions. Scans on solid  $\text{LiPF}_6$  and the electrolyte both produced endothermic peaks in this temperature range. As the  $x$  values of the  $\text{Li}_x\text{NiO}_2$  decreased, a gradual increase in reactivity was observed. A highly exothermic reaction occurred with  $x \leq 0.25$  having an onset temperature around 200 °C. To determine if the reaction was the result of oxidation reactions between the delithiated nickel material and the electrolyte rather than a simple decomposition of the  $\text{Li}_x\text{NiO}_2$  material, a sample of  $\text{Li}_{0.25}\text{NiO}_2$  was washed several times in DMC and vacuum-dried prior to analysis. Fig. 2 compares  $\text{Li}_{0.25}\text{NiO}_2$  with and without the washing/vacuum-drying procedure. It can be seen that the washing/vacuum-drying procedure reduced the exothermic energy significantly, from 1256 to 146 J/g. When electrolyte was reintroduced to the sample, the reactivity returned to its original value, confirming that the electrolyte was involved in the reaction. When

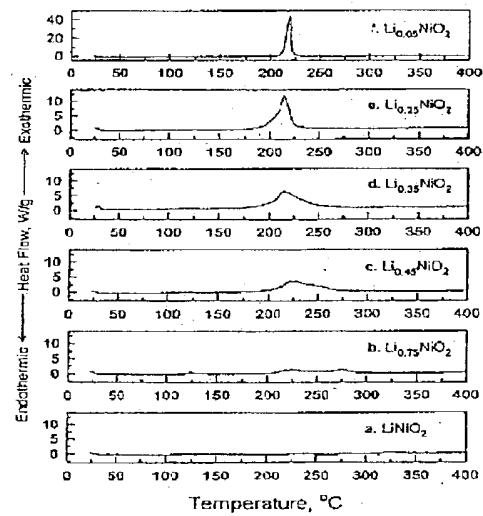


Fig. 1. DSC curves for  $\text{Li}_x\text{NiO}_2$  plus electrolyte.

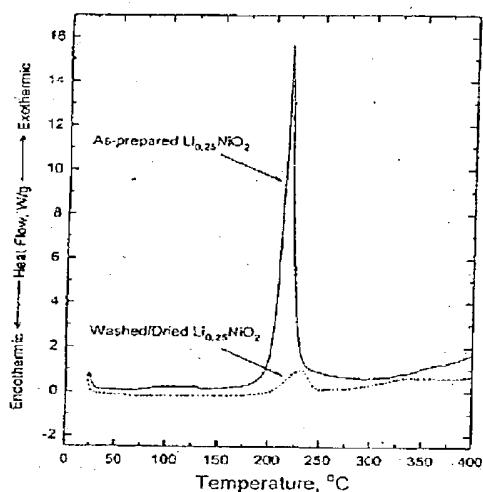


Fig. 2. DSC curves comparing  $\text{Li}_{0.25}\text{NiO}_2$  with and without a washing/vacuum-drying procedure to remove electrolyte.

EC/DMC solvent mixture was reintroduced to dried samples, the reactivity returned, but at a somewhat lower level, suggesting that both the solvents and the salt were involved in the reactions. Further work will be necessary to quantify their relative contributions.

Fig. 3 shows the results of similar experiments with  $\text{Li}_x\text{CoO}_2$  plus electrolyte. The onset temperature of the

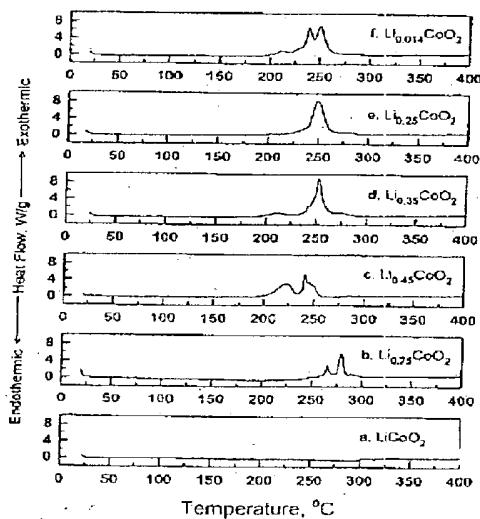


Fig. 3. DSC curves for  $\text{Li}_x\text{CoO}_2$  plus electrolyte.

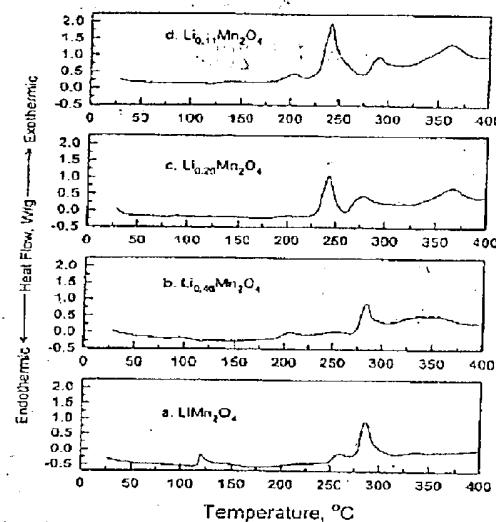


Fig. 4. DSC curves for  $\text{Li}_x\text{Mn}_2\text{O}_4$  plus electrolyte.

major exothermic peak was about 230 °C, slightly higher than that of  $\text{Li}_x\text{NiO}_2$ . Split exothermic peaks were generally observed, suggesting possible slower reaction kinetics. In general, the thermal characteristics of  $\text{Li}_x\text{CoO}_2$  plus electrolyte were similar to  $\text{Li}_x\text{NiO}_2$  but with somewhat lower reactivity.

Fig. 4 shows similar DSC curves for  $\text{Li}_x\text{Mn}_2\text{O}_4$  plus electrolyte.  $\text{LiMn}_2\text{O}_4$  exhibited some reaction with the electrolyte starting at about 250 °C. Two peaks between 250 and 300 °C were observed. For  $\text{Li}_{0.2}\text{Mn}_2\text{O}_4$ , the onset temperature shifted to a lower temperature of 225 °C and an additional peak starting at 325 °C was also observed.

The overall heat generation under the exothermic peaks is a direct indication of the reactivity between the active materials and the electrolyte. Fig. 5 summarizes the data as a function of charge capacity. It shows that highly delithiated  $\text{Li}_x\text{NiO}_2$  was the most reactive material.  $\text{Li}_x\text{CoO}_2$  was slightly less reactive than  $\text{Li}_x\text{NiO}_2$ , while the reactivity of  $\text{Li}_x\text{Mn}_2\text{O}_4$  was the lowest and the least sensitive to changes in  $x$ . The nearly linear increase in reaction energy as a function of the charging states of the oxide materials suggests that the reaction amplitude depends on the available  $\text{M}^{4+}$ , particularly where  $\text{M} = \text{Ni}$  or  $\text{Co}$ , and that  $\text{Mn}^{4+}$  exhibits less oxidation capability relative to the others. Although  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{CoO}_2$  can be charged to low  $x$  values and produce high cell capacities, the results here suggest that this will result in a significant penalty in overall cell safety.

Fig. 6 shows typical DSC curves for MCMB25-28 carbon plus electrolyte. The unintercalated sample showed

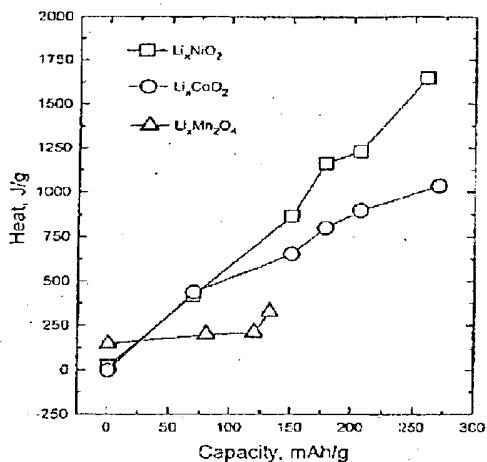


Fig. 5. Overall heat generation of the three lithium transition metal oxides as a function of charge capacity.

only the electrolyte endothermic peak at about 270 °C, which was also observed for  $\text{LiNiO}_2$  and  $\text{LiCoO}_2$ . After charging to a capacity of 85 mAh/g ( $\text{Li}_{0.23}\text{C}_6$ ), 170 mAh/g ( $\text{Li}_{0.16}\text{C}_6$ ) and 340 mAh/g ( $\text{Li}_{0.91}\text{C}_6$ ), all these intercalated samples exhibited a small exothermic reaction with a low onset temperature of about 130 °C. However, the heat associated with these peaks was small (44, 26 and 41 J/g, respectively, for this series), and independent of the  $x$  values in  $\text{Li}_x\text{C}_6$ . Over many experiments, the maxi-

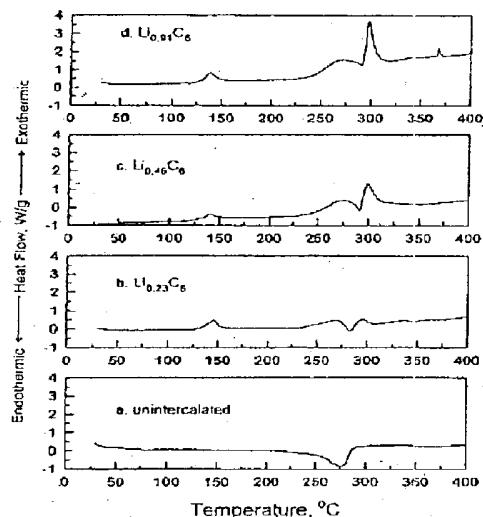


Fig. 6. DSC curves for  $\text{Li}_x\text{C}_6$  plus electrolyte.

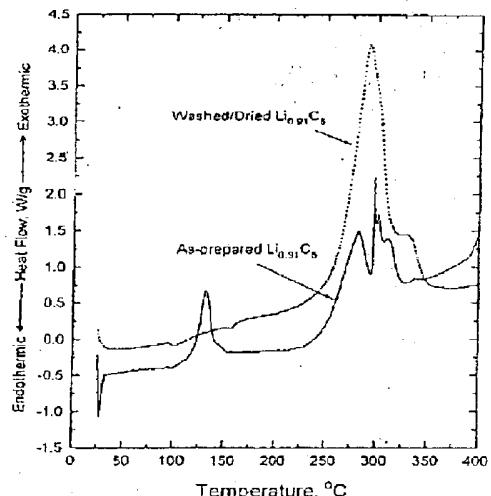


Fig. 7. DSC curves comparing  $\text{Li}_{0.91}\text{C}_6$  with and without a washing/vacuum-drying procedure to remove electrolyte.

imum value observed was 120 J/g. The data suggest that these peaks were therefore related to the surface passivation of the lithiated carbon materials. With all the Li-intercalated samples, a second broad peak was observed starting at 230 °C and the reaction heat increased as  $x$  increased. This peak appeared to be superimposed with the electrolyte endothermic peak and, thus, the resulting net heat generation was not very high. For example, the integrated heat for the fully intercalated sample  $\text{Li}_{0.91}\text{C}_6$  was about 360 J/g compared with a maximum of 1600 J/g for the  $\text{Li}_x\text{NiO}_2$  samples. The exothermic peaks for the carbon samples were also broader, spanning a 100 °C range (a 10 min interval). This relatively slow reaction might be related to slow diffusion of Li out of the MCM25-28 lattice.

Fig. 7 compares  $\text{Li}_{0.91}\text{C}_6$  with and without the washing/vacuum-drying procedure. The peak at 130 °C disappeared after the washing/vacuum-drying procedure (and came back after reintroducing electrolyte), but the higher temperature peak remained and increased somewhat in magnitude. The increase may have been due to the absence of the electrolyte endothermic decomposition and evaporation. Very recent DSC data have indicated that the high temperature peak may be the result of reactions between the PVDF binder and Li.

#### 4. Conclusions

DSC has proven to be a useful technique to study the reactivity of active materials used in Li-ion cells. The

present study indicated significant exothermic reaction between commonly used cathode materials and electrolytes. The reactions appeared to be due to contributions from the solvents, and possibly the salt. Both  $\text{Li}_x\text{NiO}_2$  and  $\text{Li}_x\text{CoO}_2$  exhibited strong reactivity with onset temperatures in the 200 to 230 °C range as  $x$  was decreased, suggesting that control of the stoichiometry of these materials is very important for achieving system safety. In contrast,  $\text{Li}_x\text{Mn}_2\text{O}_4$  reaction occurred at about 225 °C with less energy and less sensitivity to changes in  $x$ . Li-intercalated carbon in the presence of electrolyte produced DSC exotherms in two temperature ranges. The first was a low energy peak with onset temperature at approximately 130 °C, which appeared to be due to surface passivation of the lithiated carbon materials. The second peak started at about 230 °C and may have involved the PVDF binder material of the electrodes. Further work is underway to determine the mechanisms responsible for the exothermic reactions for both the cathode and the anode materials. Data of this nature are invaluable in the design of safe, high energy density electrochemical systems.

#### Acknowledgements

The authors gratefully acknowledge the US Army Communications-Electronics Command for their support of this work conducted at Rayovac Corporation.

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0026-8941/85/1214-0173/\$15.00/0  
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35 [ "POLYANILINE": INTERCONVERSION OF METALLIC AND  
INSULATING FORMS ]

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WU-SONG HUANG, SHAO-LIN MU, NANAYAKKARA (D. D. SOMASIRI,  
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**Abstract** "Polyaniline" has been synthesized in various forms both chemically and electrochemically in aqueous media. The quinoid-benzenoid-diimine form, an insulator, is doped by dilute aqueous protonic acids to the metallic regime ( $\sigma = 5 \text{ ohm}^{-1}\text{cm}^{-1}$ ; compressed pellet) to give the corresponding iminium salt. This represents a new type of p-doping phenomenon in a conducting polymer. Both these forms are stable in the presence of air and/or water. The doping process is reversed by treatment with aqueous alkali. Cyclic voltammetry studies in an aqueous electrolyte show excellent reversibility between selected reduced and oxidized forms of polyaniline.

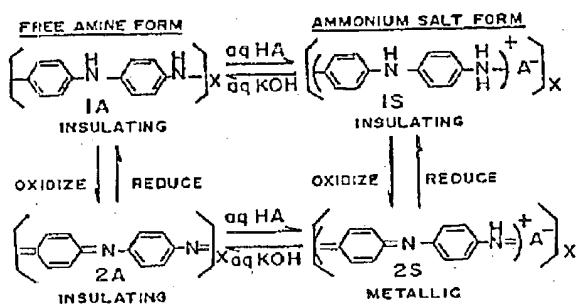
#### INTRODUCTION

"Polyaniline" has been described in many papers<sup>1</sup> during the past approximately 100 years in various, usually ill-defined forms such as "aniline black", "emeraldine", "nigraniline", etc., synthesized by the chemical or electrochemical oxidation of aniline,  $(\text{C}_6\text{H}_5)\text{NH}_2$ . The present study involves an investigation of some of the different forms in which polyaniline may exist and also its novel p-doping to the metallic regime by a simple acid/base reaction involving no formal oxidation of the polymer.

#### CONSTITUTION OF POLYANILINE

We believe polyaniline can be prepared in the four idealized forms given below, at least when its synthesis and any subsequent treatment are carried out in aqueous media. The polymers in the left-hand column are considered as being derived from the amine, 1A

(A = amine), and are hence designated (in increasing degree of oxidation) as 1A and 2A.



These forms may be interconverted at will by chemical and/or electrochemical oxidation or reduction. The chemical or electrochemical oxidation of 1A to 2A involves the reaction:

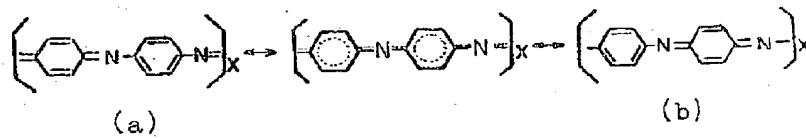


The materials in the right-hand column are regarded as being derived from the ammonium salt; 1S (S = salt), and are hence designated (in increasing degree of oxidation) as 1S and 2S. These forms may also be interconverted at will by chemical and/or electrochemical oxidation or reduction.

Preliminary electrochemical studies suggest that it may be possible to oxidize both the 2A and 2S forms further to forms 3A and 3S i.e., to  $[(=C_6H_4)=N-(C_6H_4)-N=]^{y+}A^-_x$  and  $[(=C_6H_4)=N-(C_6H_4)-N(H)=]^{(y+1)+}A^-_{(y+1)}_x$  respectively. These 3A and 3S forms must remain as speculative only, until they have been characterized.

A given "A" form, e.g. 1A, may be converted to a given "S" form, e.g. 1S, by treatment with an aqueous protonic acid, such as HCl. The acid may be removed to regenerate the "A" form by treating the "S" form with an aqueous solution of a base such as KOH. Elemental analysis of form 2S shows that even when form 2A is treated with concentrated (10 molar) aqueous HCl that only one of the two N atoms in the monomer unit is protonated. This is not surprising since in a weak base containing two N atoms, protonation of the first N atom is expected to be easier than protonation of the second.

Form 2A is of particular interest since, like  $(CH)_x$ , it appears to have a degenerate ground state, (a) and (b), viz.,



and hence it might exhibit defect states in the form of solitons.

## POLYANILINE

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SYNTHESIS OF POLYANILINE

In the present investigation polyaniline was synthesized chemically as a dark blue/black powder,  $[=(C_6H_4)=N-(C_6H_4)-N(H)=]^+Cl^-]_x$ , (form 2S) by treating a 1 molar solution of aqueous HCl containing dissolved aniline, with the oxidizing agent ammonium peroxydisulfate,  $(NH_4)_2S_2O_8$ . Protonation was completed by washing the powder with 1 molar aqueous HCl followed by drying under a dynamic vacuum ( $\sim 10$  microns) at room temperature for several days to remove water and HCl. After this time the conductivity (compressed pellet; four probe) had decreased to a constant value of  $\sim 5 \text{ ohm}^{-1} \text{ cm}^{-1}$ . Elemental analysis of several samples (e.g., %C + %H + %N + %Cl = 97.5%; 0%S) showed that a maximum of one HCl combined with each monomer repeat unit (containing two N atoms). Nonvolatile acids such as  $H_2SO_4$  should not be used in any stage in the synthesis as a substitute for HCl since upon removal of the water under vacuum a thin film of concentrated  $H_2SO_4$  will remain on the particles of the powder.

The 2S form can be converted to the 2A form, a dark purple/black powder exhibiting a copper glint ( $\sigma$ , 2 probe of compressed copper-colored pellet,  $\sim 10^{-11} \text{ ohm}^{-1} \text{ cm}^{-1}$ ) by stirring with a 0.5 molar solution of KOH in a water/methanol mixture followed by washing with a water/methanol mixture and drying under a dynamic vacuum. Elemental analysis shows that essentially all the HCl is removed by this procedure. For example, in one preparation only 0.04 mole of HCl remained for every mole of monomer repeat unit (%C + %H + %N + %Cl = 97.37%; S, "trace").

Excellent cohesive dark green films of form 2S (containing fluoroborate anion) were synthesized electrochemically on Pt foil in 5 ml of 48% aqueous  $HBF_4$  containing 1 ml of aniline and 10ml of distilled water. Successive increments of 0.05V were applied between two Pt electrodes (each  $1 \text{ cm}^2$ ; 1 cm apart) until a potential of 0.75V was reached. The current was not permitted to rise above 1 mA. The potential was then held at this value (anode potential 0.72V vs. SCE, NaCl salt bridge) for 20 hours and the anode on which the film (ca. 3 mg.) had been deposited was washed with 16% aqueous  $HBF_4$  and dried under dynamic vacuum. Free standing films can be prepared using a conducting glass anode. The I/R spectra of the chemically and electrochemically synthesized forms of 2S were identical except for differences attributed to the different anions.

Form 2A may be reduced to form 1A chemically by a reducing agent such as hydrazine,  $N_2H_4$ , or electrochemically at a potential of  $\sim 0.8$ V. (vs.  $Zn^{+2}/Zn$ ). The electrochemically prepared 1A exists as a very pale yellow, semitransparent thin film.

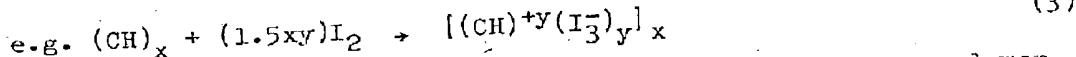
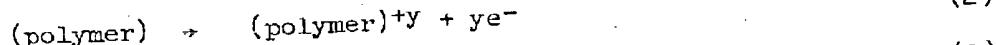
PROTONIC ACID DOPING

The conventional method of p-doping (oxidizing) an organic polymer

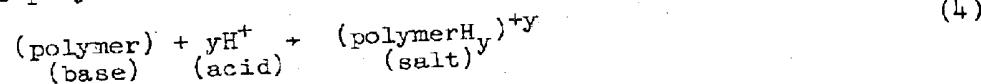
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176 involves removal of electrons from the pi system of the polymer by chemical or electrochemical oxidation:

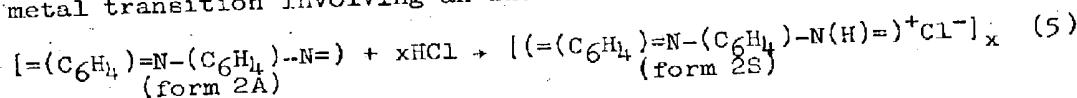


In principle it should be possible to p-dope a conducting polymer by adding a proton, which may interact with and hence partly depopulate the pi system with concomitant increase in conductivity of the polymer:



This is a simple acid/base interaction, in which no formal oxidation or reduction occurs. Form 2A is washed with an aqueous

We have found that when form 2A is washed with an aqueous protonic acid such as HCl or HBF<sub>4</sub> it undergoes an insulator-metal transition involving an increase in conductivity of ~ 10<sup>11</sup>:



This transition is readily reversed by treatment with aqueous base. The conductivity of form 2A to the

The extreme sensitivity of the conductivity of form 2A to the pH of the aqueous HCl solution with which it is equilibrated is illustrated in Figure 1.

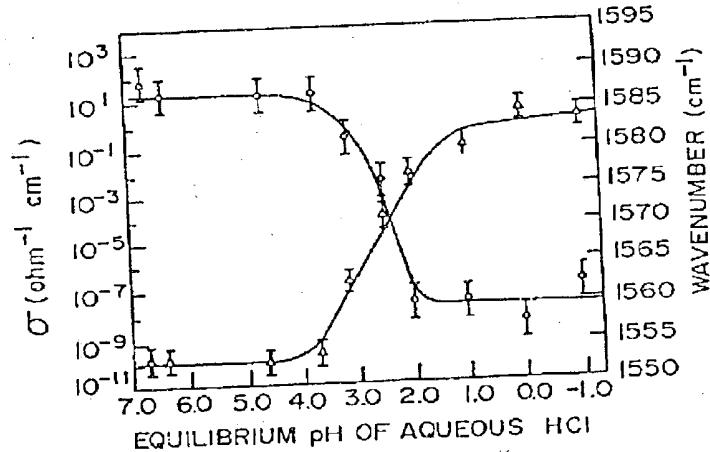


FIGURE 1. Relationship between the final (equilibrium) pH of the aqueous HCl with which polyaniline (form 2A) is washed and (1) the conductivity of the resulting dried powder, ( $\Delta$ ); (2) the frequency of the ring breathing absorbance, ( $\circ$ ), of the dried powder.

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Each data point gives the conductivity of a ~ 250 mg sample of form 2A after it had been stirred with 500 ml of aqueous HCl of various selected concentrations. After 55 hours the pH of the solution was measured, the resulting polyaniline powder was dried under dynamic vacuum for 24-72 hours and its conductivity, I/R spectra and elemental composition were determined.

The relationship between the conductivity of selected samples and the percent doping is given in Figure 2. Since each HCl molecule which reacts with form 2A is associated with a Cl<sup>-</sup> ion, the (Cl:N ratio) · 100 will represent the percent of the N atoms which are protonated, i.e. will represent the percent doping. The curve given in Figure 2 is characteristic of conventional doping of a conducting polymer, i.e., the conductivity rises rapidly at the beginning of the doping process and then shows little change even though the polymer becomes more highly doped.

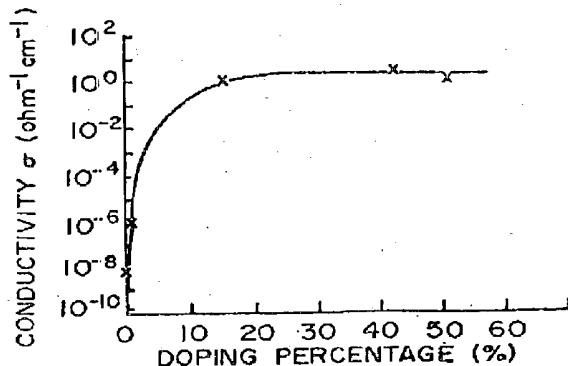
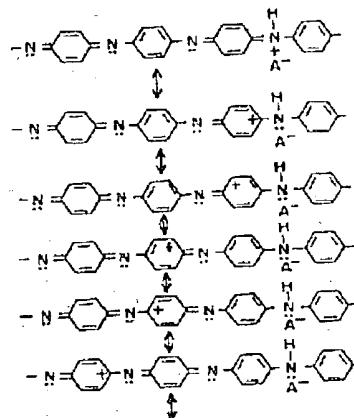


FIGURE 2 Relationship between the conductivity of polyaniline (form 2A) and percentage of protonation, i.e. percentage doping.

Also shown in Figure 1 is the change in the frequency of the I/R (C<sub>6</sub>H<sub>4</sub>) ring breathing absorbance. As can be seen, the frequency of this absorbance decreases as the conductivity increases. If the proton should interact and partly depopulate the pi system of the polymer the frequency of this mode may decrease with increasing protonation since the C-C bond order (and hence, force constant) in the (C<sub>6</sub>H<sub>4</sub>) ring decreases with decreasing population of the bonding pi orbitals. As can be seen from the classical resonance forms of form 2S given below, it is to be expected that positive charge will be transferred in part from the N to the pi system of the (C<sub>6</sub>H<sub>4</sub>) rings. This will result in a partial delocalization of positive charge along the polymer chain. The charge will naturally be pinned close to the anion, A<sup>-</sup> and delocalization will become less extensive as the distance from the N<sup>+</sup> atom increases.

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In order to obtain a more complete understanding of the oxidation/reduction relationship between the 1A and 2A forms of polyaniline, cyclic voltammetry studies (Zn reference electrode) were performed using polyaniline electrochemically deposited as a thin film on a Pt electrode as described above (see Figure 3). The electrolyte, (1.0M  $\text{ZnCl}_2$  + 0.5M  $\text{NH}_4\text{Cl}$ ) has a pH  $\sim$  4. At this pH, as can be seen from Figure 1, the polyaniline will exist predominantly in the "A" form. Potentials vs. the normal hydrogen electrode, NHE, may be obtained by subtracting 0.76V from the experimental values observed vs. the Zn reference electrode.

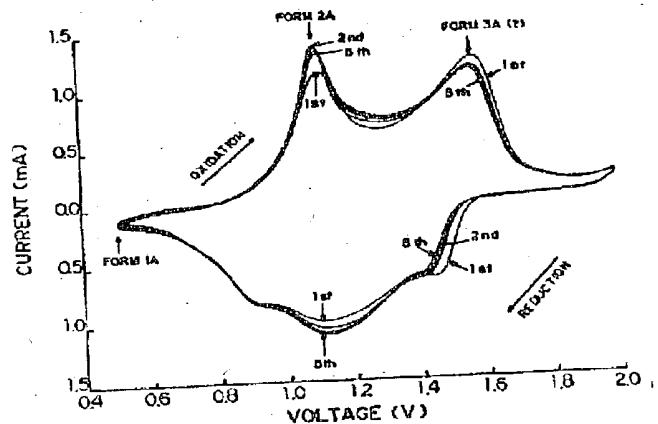


FIGURE 3 Five cyclic voltammograms between 0.50V and 2.0V (5mV/sec) of polyaniline in (1.0M  $\text{ZnCl}_2$  + 0.5M  $\text{NH}_4\text{Cl}$ ; pH  $\sim$  4) vs.  $\text{Zn}^{2+}/\text{Zn}$  reference electrode.

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It should be noted that good cyclic voltammograms are usually obtained more readily with thin films than with powders. The cyclic voltammograms described here cannot, therefore, be correlated exactly with a given form of the chemically synthesized polyaniline described above.

In the oxidation cycle the pale yellow form 1A is characterized by a potential of ~ 0.50V; a dark green form, possibly form 2A, by a peak potential at 1.10V and a dark blue form, possibly form 3A, by the potential at 1.58V. It is possible that the dark blue material characterized by the peak at 1.58V might actually be form 2A and the dark green material characterized by the peak at 1.10V might merely be partly oxidized form 1A. However, until the nature of the peak at 1.58V is clarified, the peak at 1.10V will be assumed to be characteristic of form 2A. It should be stressed that the cyclic voltammograms are very sensitive to changes in the pH of the electrolyte. The cyclic voltammograms discussed here are not necessarily characteristic of polyaniline in electrolytes other than that used in these studies.

In view of the less than ideal reversibility of the above redox processes a second set of cyclic voltammograms were obtained under identical experimental conditions using an identical film of polyaniline except that the oxidation step was arbitrarily terminated at 1.40V. These are shown in Figure 4.

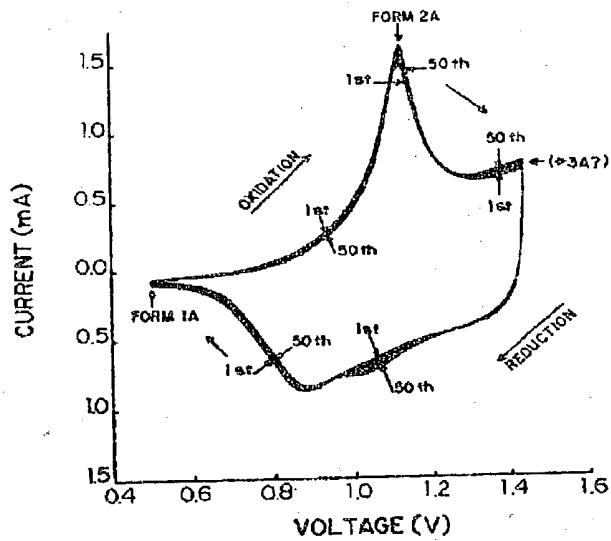


FIGURE 4 Fifty cyclic voltammograms between 0.50V and 1.40V, (5mV/sec) of polyaniline in (1.0M  $ZnCl_2$  + 0.5M  $NH_4Cl$ ; pH ~ 4) vs.  $Zn^{+2}/Zn$  reference electrode.

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It can be seen that excellent reversibility is obtained under these conditions, the coulombic capacity decreasing to only 99.1% after the 50th cycle. These observations are of importance in our battery studies described elsewhere.<sup>2</sup>

#### CONCLUSIONS

It is apparent that the diverse forms in which polyaniline may be synthesized and interconverted results in this material having a potentially large and rich chemistry, electrochemistry and physics. The novel protonic acid doping of the quinoid benzoid diimine form of polyaniline to the metallic regime is of particular experimental and theoretical interest.

#### ACKNOWLEDGEMENTS

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2. A. G. MacDiarmid, S. L. Mu, N. L. D. Somasiri and W. Wu, reported elsewhere in these proceedings.